



# Effect of pretreatment and regeneration conditions of Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts for N<sub>2</sub>O decomposition and/or reduction in O<sub>2</sub>-rich atmospheres and in the presence of NO<sub>x</sub>, SO<sub>2</sub> and H<sub>2</sub>O

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## ABSTRACT

The effect of the pretreatment (inert, oxidative, and reducing) of Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst on its activity and stability in the decomposition of N<sub>2</sub>O in the absence or presence of O<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>O and NO<sub>x</sub> was studied in the present work. Decomposition of pure N<sub>2</sub>O was slightly enhanced by the H<sub>2</sub>-pretreated catalyst (metallic Ru) compared to the O<sub>2</sub>- or He-pretreated ones, owing to a cyclic oxidation–reduction pathway of metallic Ru. The observed decrease of activity by O<sub>2</sub> or H<sub>2</sub>O addition was reversible compared to SO<sub>2</sub> which caused a strong, irreversible deactivation of the catalyst, irrespective of the type of pretreatment. This was attributed to the formation of stable sulphates, mainly those on RuO<sub>2</sub> surface, which could only be removed by regeneration under reducing (H<sub>2</sub> in He) atmosphere at temperatures of ca. 500 °C. Oxidative or inert regeneration required very high temperatures (i.e. >700 °C) in order to decompose these sulphates. A method of retaining N<sub>2</sub>O conversion activity very high (>98%) for long reaction times is suggested and is based on frequent and short-time (ca. 10 min) regenerations of the catalyst under reducing atmosphere (ca. 5% H<sub>2</sub> in He). The effect of co-feeding various reducing agents, such as CO or C<sub>3</sub>H<sub>6</sub>, on the N<sub>2</sub>O conversion activity in the presence of O<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>O and NO<sub>x</sub> is negligible, mainly because they are oxidized at relatively low temperatures in the O<sub>2</sub>-rich feeds used in this study.

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## 1. Introduction

Nitrous oxide (N<sub>2</sub>O) is a noxious gas and damages the environment seriously since it contributes significantly to the destruction of ozone in the stratosphere and is considered as a powerful greenhouse gas due to its long life time (150 years) in the atmosphere and its 310 times higher greenhouse potential with respect to CO<sub>2</sub> [1,2]. N<sub>2</sub>O continues to increase in the atmosphere at faster rates over the last 20 years mainly due to uncontrolled anthropogenic activities (typically represent about half of the total N<sub>2</sub>O emissions, the rest being natural sources), such as misuse of fertilizers in land cultivation and various polluting industrial processes [1–6]. Worldwide the chemical industry is responsible for about 15–25% of the N<sub>2</sub>O emissions [2]. The major industrial processes whose emissions contain N<sub>2</sub>O are: (a) production of nitric acid (a key raw material in the fertilizer industry), (b) production of adipic acid, caprolactam, acrylonitrile, glyoxal, and

other organic synthetic processes which use nitric acid as oxidant/reagent, and (c) combustion of fossil fuels, biomass, and waste in fluidized-bed combustors [1–6]. All the above processes contribute significantly to N<sub>2</sub>O formation but it is noteworthy to mention that in the case of adipic acid for each molecule of adipic acid one molecule of N<sub>2</sub>O is produced. As a result, the emissions of this process contain about 30–50 vol.% N<sub>2</sub>O while the typical concentration in the other processes is usually below 1 vol.% [4,6].

Various catalytic processes for the abatement of N<sub>2</sub>O from the flue gases of adipic acid plants have been successfully developed [7–10]; however, these are not applicable to nitric acid plants or combustion processes mainly due to the significantly lower concentration of N<sub>2</sub>O in the flue gases of the latter processes and the simultaneous presence of various catalyst's "poisons", such as SO<sub>2</sub> and H<sub>2</sub>O [4–6]. In general, the catalytic decomposition and the selective catalytic reduction (SCR) of N<sub>2</sub>O to N<sub>2</sub> are two candidate technologies, which can be applied to reduce the N<sub>2</sub>O emissions [11–19]. The catalytic decomposition of N<sub>2</sub>O has been investigated to a greater extent than SCR. A large variety of catalysts have been studied for the decomposition of N<sub>2</sub>O, comprising transition (Fe, Cu, Co, Ni) and noble-metal based

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catalysts (Rh, Ru, Pd) on various supports, such as metal oxides (e.g.  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{CaO}$ ,  $\text{TiO}_2$ ,  $\text{CeO}_2$ ,  $\text{Fe}_2\text{O}_3$ ), perovskites, hydro-talcites, zeolites (ZSM-5, BEA, USY, Ferrierite) and mesoporous materials (MCM-41, SBA-15) [4–16,22–35,36].

Supported Ru catalysts, especially Ru/ $\gamma$ -alumina, are known as very active catalysts for the selective catalytic reduction (SCR) of  $\text{NO}_x$  [20,21]. Because of its high activity, selectivity towards  $\text{N}_2$  and stability against sulphur poisoning, ruthenium appeared as an ideal catalyst for  $\text{deNO}_x$  applications. Li and Armor [28,29] screened a wide variety of both alumina-supported and zeolite-supported metal and metal oxide catalysts for  $\text{N}_2\text{O}$  conversion to  $\text{N}_2$  and  $\text{O}_2$ . They reported that ruthenium– together with rhodium-based catalysts gave nearly complete conversion of  $\text{N}_2\text{O}$  to  $\text{N}_2$  and  $\text{O}_2$  at relatively low temperatures (350–450 °C). It was also shown that the activity of the Ru catalysts supported on ZSM-5 and  $\gamma$ - $\text{Al}_2\text{O}_3$  declined dramatically in the presence of  $\text{O}_2$ . Zeng and Pang [30] also studied the  $\text{N}_2\text{O}$  decomposition over Ru/ $\gamma$ - $\text{Al}_2\text{O}_3$  catalysts but using relatively high concentrations of  $\text{N}_2\text{O}$  in the feed (~28 vol.%). They observed that the catalytic activity was inhibited by both  $\text{O}_2$  and  $\text{H}_2\text{O}$ . However, Wang and Zeng [31] showed that the negative effect of  $\text{H}_2\text{O}$  on the activity of Ru/ $\gamma$ - $\text{Al}_2\text{O}_3$  catalysts was minimized at relative high reaction temperatures (>470 °C), probably due to enhanced desorption of water from the active sites at those temperatures. In our previous work [32] the effect of  $\text{SO}_2$  and  $\text{H}_2\text{O}$  addition in an  $\text{O}_2$ -rich feed, on the  $\text{N}_2\text{O}$  decomposition with Ru/ $\gamma$ - $\text{Al}_2\text{O}_3$  catalyst was studied. A shift of the  $\text{N}_2\text{O}$  conversion vs. temperature curves towards higher temperatures was observed when  $\text{SO}_2$  and  $\text{H}_2\text{O}$  were added, either separately or simultaneously, in the feed. The inhibition caused by  $\text{SO}_2$  was attributed to the formation of sulphates, while that caused by water to the competitive chemisorption of  $\text{H}_2\text{O}$  and  $\text{N}_2\text{O}$  on the same active sites. Despite that many studies have identified the “poisoning” effect of  $\text{SO}_2$  [4,5,23], there are some recent results which show that  $\text{SO}_2$  can actually promote the direct decomposition of  $\text{N}_2\text{O}$ , at least for the iron-based zeolitic catalysts studied in the respective work [37].

Pinna et al. [34] suggested that the oxidized Ru on  $\text{ZrO}_2$  support was more active at lower temperature compared to the reduced samples which required an induction period to achieve a stable conversion associated with the oxidation of Ru active sites. More recently Reddy et al. [33] reported the high activity of Ru/ $\gamma$ - $\text{Al}_2\text{O}_3$  catalysts prepared by deposition–precipitation method in the decomposition of  $\text{N}_2\text{O}$  and attributed this activity to the cationic Ru species that formed with that method. Kawi et al. [35] studied the catalytic decomposition and reduction of  $\text{N}_2\text{O}$  over various Ru/MCM-41 catalytic materials. They found that the Ru/MCM-41 (5 wt.% Ru) catalyst prepared with  $\text{Ru}(\text{OH})_3$  was the most active for the catalytic decomposition of  $\text{N}_2\text{O}$ , achieving a complete decomposition of  $\text{N}_2\text{O}$  at 400 °C. The catalyst activity was significantly enhanced when CO was introduced in the feed stream and complete conversion of  $\text{N}_2\text{O}$  was achieved at 300 °C. On the contrary, the presence of moisture and oxygen decreased the catalyst activity, due to the competitive adsorption between these species and  $\text{N}_2\text{O}$  on the catalytic sites.

In the present study we investigate systematically the effect of the pretreatment (inert, oxidative, reducing atmosphere) of Ru/ $\gamma$ - $\text{Al}_2\text{O}_3$  catalyst on its catalytic activity and stability in the decomposition of  $\text{N}_2\text{O}$  in the absence or presence of  $\text{O}_2$ ,  $\text{SO}_2$  and  $\text{H}_2\text{O}$ . The effect of co-presence of  $\text{NO}_x$  and  $\text{N}_2\text{O}$  in the feed was also studied. Furthermore, we investigated the possible regeneration of partially deactivated Ru/ $\gamma$ - $\text{Al}_2\text{O}_3$  catalysts and we developed a methodology for retaining catalyst's activity at very high levels for long reaction times by applying short-term regeneration steps. Finally, we studied the effect of co-feeding various reducing agents, such as CO or  $\text{C}_3\text{H}_6$ , on the  $\text{N}_2\text{O}$  conversion activity.

## 2. Experimental

### 2.1. Materials

$\gamma$ - $\text{Al}_2\text{O}_3$  extrudates supplied by Engelhard (sample code: Al-3992 E 1/8 in.) were used as the catalyst support. The extrudates were crushed and sieved in order to obtain fraction of particles with size 180–355  $\mu\text{m}$ . Ru (2 wt.% on total catalyst weight) was loaded on  $\gamma$ - $\text{Al}_2\text{O}_3$  by the dry impregnation method using aqueous solution of  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  (Next Chimica). The catalyst was then dried at 120 °C for 2 h and calcined in air at 500 °C for 4 h prior to characterization and testing.

### 2.2. Catalyst characterization

Powder X-ray diffraction (XRD) measurements of the catalysts were performed using a Siemens D 500 X-ray Diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ , 40 kV, 40 mA). The patterns were recorded in the 2-theta ( $2\theta$ ) range from 5° to 85° in steps of 0.04° and with counting time 2 s per step. Scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) was performed using a JEOL JSM-6300 Scanning Microscope equipped with an X-ray micro-analyzer (Oxford ISIS 2000). EDS microanalysis was used for the determination of the relative content of S in the fresh-calcined, partially deactivated and regenerated catalysts. Sulphur (S) elemental analysis was also performed using a CHNS-932 analyzer (LECO).

The reducibility of the catalysts was studied by temperature programmed reduction with  $\text{H}_2$  (TPR- $\text{H}_2$ ). In a typical experiment, 0.2 g of the sample were loaded in a U-shaped quartz reactor and pretreated at 500 °C in 5%  $\text{O}_2/\text{He}$  for 1 h, followed by cooling to 40 °C. The sample was then heated from 40 to 800 °C at a heating rate of 10 °C/min in a 5%  $\text{H}_2/\text{He}$  flow (75  $\text{cm}^3/\text{min}$ ). The composition of the exit gas was monitored on-line by a quadrupole mass analyzer (Omnistar, Balzers). The main  $m/z$  fragments registered were  $\text{H}_2 = 2$ ,  $\text{H}_2\text{O} = 18$ ,  $\text{He} = 4$ . Temperature programmed desorption experiments coupled with mass spectroscopy (TPD-MS) were also conducted on selected catalyst samples using the same set-up as above, from 25 to 900 °C under He flow, in order to identify the various desorbed species from the used and regenerated catalyst samples.

### 2.3. Catalytic reaction/analysis system

All catalytic experiments were performed in a bench-scale reaction unit that consists of the feed gas system, a fixed bed tubular reactor (i.d.: 0.7 cm) made of quartz, a three-zone furnace controlled by PID controllers and the on-line gas analysis system which comprised a chemiluminescence's  $\text{NO}/\text{NO}_2/\text{NO}_x$  analyzer (42C-HL, Thermo Environmental), a non-dispersive infrared CO and  $\text{CO}_2$  analyzer (NGA 2000, Rosemount), a magnetopneumatic  $\text{O}_2$  analyzer (MPA-510, Horiba), a  $\text{N}_2\text{O}$  analyzer (VIA-510, Horiba) and a  $\text{SO}_2$  analyzer (NGA 2000, Rosemount). In a typical  $\text{N}_2\text{O}$  decomposition experiment the fixed bed reactor was loaded with 0.5 g of catalyst which was first treated at 600 °C for 1 h in an inert (He) or reducing (5%  $\text{H}_2/\text{He}$ ) or oxidative (5%  $\text{O}_2/\text{He}$ ) atmosphere (total flow rate 100  $\text{cm}^3/\text{min}$ ). The composition of the feed was either 500 ppm  $\text{N}_2\text{O}$  or 500 ppm  $\text{N}_2\text{O}$  and 5%  $\text{O}_2$  or 500 ppm  $\text{N}_2\text{O}$ , 5%  $\text{O}_2$ , 10%  $\text{H}_2\text{O}$  and 50 ppm  $\text{SO}_2$ . The effect of simultaneous presence of  $\text{NO}_x$  in the feed was also tested (500 or 1000 ppm  $\text{NO}_x$ ). The catalysts were activated prior to measurements by increasing the temperature from 250 to 600 °C under reaction feed and holding at 600 °C for 30 min. Measurements were then taken downwards from 600 to 250 °C every 20 °C after 30 min stabilization at each reaction temperature. The contact time, W/F, defined as the ratio of catalyst weight to total flow rate was 0.06 g s/ml (corresponding GHSV  $\cong 56,000 \text{ h}^{-1}$ ).

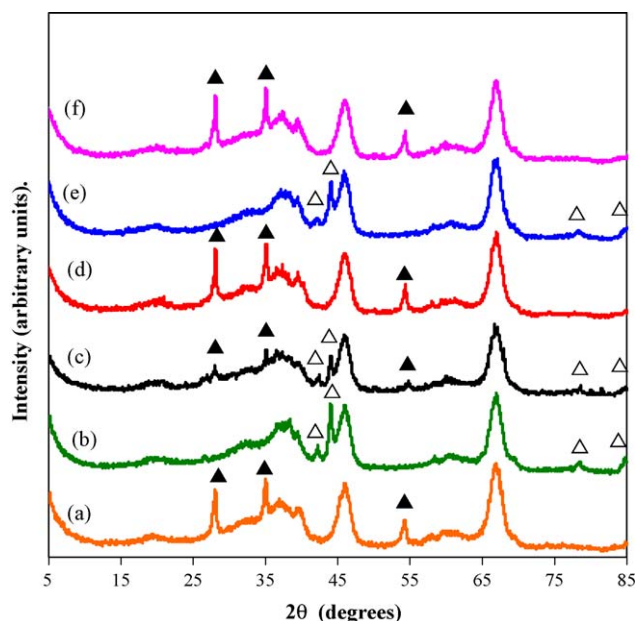
Stability of catalysts' performance (time-on-stream) was tested at 500 °C using 1 g of catalyst (loaded on a tubular reactor with i.d. of 1.8 cm) and a feed with composition of 500 ppm N<sub>2</sub>O, 5% O<sub>2</sub>, 10% H<sub>2</sub>O and 50 ppm SO<sub>2</sub> with or without 500 or 1000 ppm NO<sub>x</sub> (feed total flow rate 500 cm<sup>3</sup>/min; W/F = 0.12 g s/ml; GHSV  $\cong$  19,500 h<sup>-1</sup>). Intermediate short-term (8–30 min) regeneration of the partially deactivated catalysts was performed at 500 °C under inert, oxidative or reducing atmosphere. The conversion (selective catalytic reduction and/or decomposition) of N<sub>2</sub>O in the presence of C<sub>3</sub>H<sub>6</sub> or CO as reductants was also investigated using 0.5 g of catalysts in a 0.7 cm i.d. tubular reactor and various feeds, as in the N<sub>2</sub>O decomposition tests described above (feed total flow rate 500 cm<sup>3</sup>/min, W/F = 0.06 g s/ml; GHSV  $\cong$  56,000 h<sup>-1</sup>).

### 3. Results and discussion

#### 3.1. Catalyst characterization

The various catalyst samples derived from the different pretreatments of 2 wt.% Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were studied by XRD measurements in order to identify the oxidation state and size of Ru particles. Representative XRD patterns are shown in Fig. 1. Calcination of the catalyst after impregnation with ruthenium salt and drying, resulted in the formation of oxidized Ru as verified by the presence of diffraction peaks at 28°, 35° and 54° 2 $\theta$  which are characteristic of the RuO<sub>2</sub> phase (Fig. 1a). Further pretreatment (prior to reaction) under reductive atmosphere led to the formation of metallic Ru particles as verified by the characteristic diffraction peaks at 42°, 44° and 78° 2 $\theta$  (Fig. 1b) while inert or oxidative pretreatment had no additional effect on oxidized Ru. The particle/crystal size for RuO<sub>2</sub> and metallic Ru was estimated to  $\sim$ 22 nm from Scherrer analysis of the diffraction peaks at 35° 2 $\theta$  (Fig. 1a) and 44° 2 $\theta$  (Fig. 1b), respectively.

Fig. 1 shows also the XRD patterns of the catalyst samples after reaction and consequent regeneration (these results are discussed in following paragraphs).

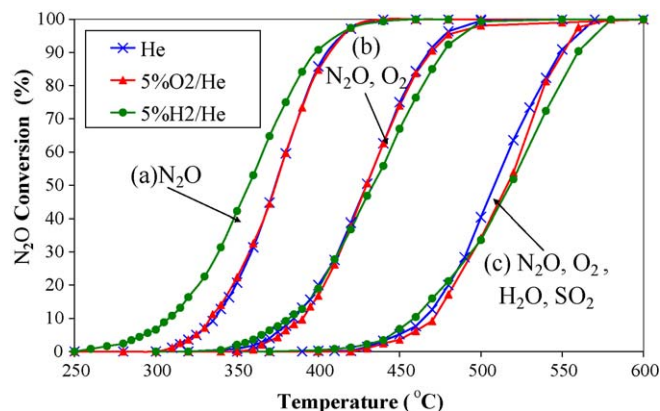


**Fig. 1.** XRD patterns for the catalyst samples: (a) Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (after impregnation and drying) calcined at 500 °C for 4 h in air, (b) Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> pretreated at 600 °C for 1 h with 5% H<sub>2</sub>/He, (c) Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> pretreated at 600 °C for 1 h with 5% H<sub>2</sub>/He followed by reaction with N<sub>2</sub>O/He at 500 °C for 4 h, (d) Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> after 4 h reaction at 500 °C with N<sub>2</sub>O/O<sub>2</sub>/SO<sub>2</sub>/H<sub>2</sub>O/He, (e) partially deactivated Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (sample d) regenerated with 5% H<sub>2</sub>/He (f) partially deactivated Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (sample d) regenerated with 5% O<sub>2</sub>/He. RuO<sub>2</sub> phase (▲) and metallic Ru phase (△).

#### 3.2. Effect of catalyst's pretreatment procedure

A parameter that plays important role in the overall catalytic performance is the catalyst's pretreatment procedure that takes place prior to the reaction. In the present study the Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts, following the initial calcination in air after impregnation, were treated *in situ* in the reactor at 600 °C under inert or reducing or oxidative atmosphere, as explained in the experimental section. The catalytic activity in N<sub>2</sub>O decomposition of the Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts pretreated under the different atmospheres is shown in Fig. 2 as % N<sub>2</sub>O conversion versus reaction temperature curves. Three types of feed were tested: (a) N<sub>2</sub>O, (b) N<sub>2</sub>O and O<sub>2</sub>, and (c) N<sub>2</sub>O, O<sub>2</sub>, SO<sub>2</sub> and H<sub>2</sub>O. Typical sigmoid-type curves were observed in all cases. In general, the effect of catalyst's pretreatment was not significant, except in the experiments of pure N<sub>2</sub>O decomposition where the reducing pretreatment induced slightly higher activity. The XRD measurements of the catalysts (Fig. 1) showed that the H<sub>2</sub>-pretreated sample exhibited peaks attributed to only metallic Ru (Fig. 1b) while the same sample after 4 h reaction with N<sub>2</sub>O/He at 500 °C showed the characteristic peaks of both metallic and oxidized state of Ru (Fig. 1c). It can thus be suggested that metallic Ru is slightly more active compared to fully oxidized Ru, via the previously suggested cyclic oxidation-reduction mechanism in which metallic Ru is partially oxidized by subtracting the atomic oxygen from N<sub>2</sub>O (which is converted to N<sub>2</sub>), while at a next step, this surface oxygen atom can desorb by combination with another oxygen atom or by direct reaction with another N<sub>2</sub>O molecule [5]. Addition of relatively high amount of oxygen in the feed (5%) inhibited the reaction, independently of the pretreatment procedure, since all curves were shifted to higher temperatures. This excess of O<sub>2</sub> fully oxidized the H<sub>2</sub> pretreated sample during the activation step, thus rendering it comparable to the other two samples which were oxidized prior to contact with the reaction feed. Light-off temperature (at which 50% of N<sub>2</sub>O conversion is reached) was approximately 60 °C higher compared to the experiments in the absence of O<sub>2</sub>. Inhibition by oxygen can be simply accounted for by the reversible dissociative adsorption of oxygen either directly or via molecular adsorption of oxygen which occurs over metal surfaces [5]. Consequently, O<sub>2</sub> has only a reversible effect, due to competitive adsorption, and does not irreversibly deactivate the catalyst, since after removal of O<sub>2</sub> from the feed (in the experiments of Fig. 2) the % conversion of pure N<sub>2</sub>O returned to the initial level that corresponds to the performance of the oxidized catalysts.

A more pronounced inhibition was caused by the addition of "poisonous" gases (SO<sub>2</sub> and H<sub>2</sub>O) together with O<sub>2</sub> in the feed,



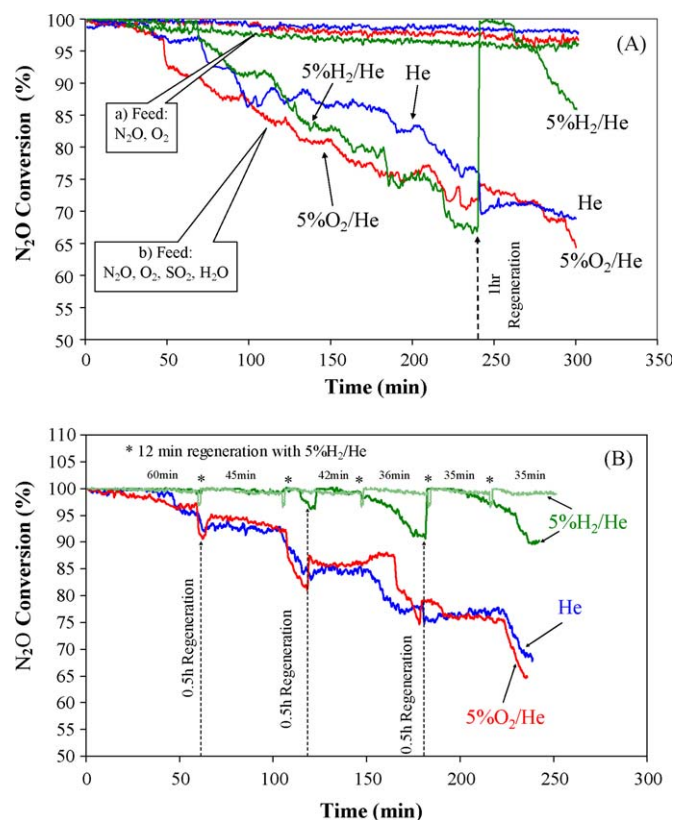
**Fig. 2.** Effect of the pretreatment procedure of Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst on N<sub>2</sub>O decomposition activity for various feeds: (a) 500 ppm N<sub>2</sub>O in He, (b) 500 ppm N<sub>2</sub>O, 5% O<sub>2</sub> in He, and (c) 500 ppm N<sub>2</sub>O, 5% O<sub>2</sub>, 50 ppm SO<sub>2</sub>, 10% H<sub>2</sub>O in He. Total flow rate: 500 cm<sup>3</sup>/min; catalyst weight: 0.5 g; GHSV: 56,000 h<sup>-1</sup>. Type of pretreatment: (x) inert, (▲) oxidative, (●) reducing.



independently of the pretreatment procedure, since all curves were shifted to even higher temperatures (light-off temperature was approximately 100 °C higher compared to the experiments with feed containing only N<sub>2</sub>O and O<sub>2</sub>). Nevertheless, 100% conversion of N<sub>2</sub>O was reached at about 575 °C in the presence of all reactant gases (Fig. 2). Water separately had also an inhibition effect, due to the competitive adsorption of H<sub>2</sub>O and N<sub>2</sub>O molecules on the same active sites. However, this inhibition effect caused by H<sub>2</sub>O was completely reversible and the catalyst's initial activity for the decomposition of pure N<sub>2</sub>O was restored after removing H<sub>2</sub>O from the feed, as in the case of O<sub>2</sub>. On the other hand the deactivation caused by SO<sub>2</sub> was irreversible, as it has been also shown in previous reports [4,5,23,32] and attributed to the formation of stable sulphates on the surface of metal oxides and oxidic supports. The formation of these sulphates was also verified in the present work by conducting TPD-MS and TPR-H<sub>2</sub> experiments on the deactivated catalysts (see Fig. 4 and related discussion below).

### 3.3. Effect of time-on-stream and regeneration treatment

The effect of time-on-stream on catalyst's activity was tested for two types of feeds: (a) N<sub>2</sub>O and O<sub>2</sub>, (b) N<sub>2</sub>O, O<sub>2</sub>, SO<sub>2</sub> and H<sub>2</sub>O, at 500 °C. Fig. 3A shows the % N<sub>2</sub>O conversion versus time-on-stream



**Fig. 3.** (A) Effect of pretreatment of Ru/γ-Al<sub>2</sub>O<sub>3</sub> catalyst on % N<sub>2</sub>O conversion vs. time-on-stream, in O<sub>2</sub>-rich feed and in the absence or presence of SO<sub>2</sub> and H<sub>2</sub>O. (a) Feed: 500 ppm N<sub>2</sub>O, 5% O<sub>2</sub> in He, and (b) feed: 500 ppm N<sub>2</sub>O, 5% O<sub>2</sub>, 50 ppm SO<sub>2</sub>, 10% H<sub>2</sub>O in He (reaction temperature: 500 °C; total flow rate: 500 cm<sup>3</sup>/min; catalyst weight: 1 g; GHSV: 19,500 h<sup>-1</sup>). After 240 min of time-on-stream with feed (b) catalyst samples were regenerated for 1 h under the atmosphere used for pretreatment, followed by reaction with the same feed. (B) Reaction-regeneration cycles (60 min reaction, 30 min regeneration) of Ru/γ-Al<sub>2</sub>O<sub>3</sub> catalyst. Effect of regeneration treatment on % N<sub>2</sub>O conversion vs. time-on-stream (feed: 500 ppm N<sub>2</sub>O, 5% O<sub>2</sub>, 10% H<sub>2</sub>O, 50 ppm SO<sub>2</sub> in He; reaction temperature: 500 °C; total flow rate: 500 cm<sup>3</sup>/min; catalyst weight: 1 g; GHSV: 19,500 h<sup>-1</sup>). In a second series of experiments, repeated regeneration with 5% H<sub>2</sub>/He for 12 min was performed (indicated by asterisk) as soon as conversion of N<sub>2</sub>O reached 98%.

curves for the three catalyst samples pretreated under different atmospheres (inert, oxidative and reducing). It can be seen that in the absence of SO<sub>2</sub> and H<sub>2</sub>O the % conversion of N<sub>2</sub>O in O<sub>2</sub>-rich feed (5% O<sub>2</sub>) was stable (>95%) for more than 6 h of operation, while the different type of pretreatment had a minor effect on activity. However, when SO<sub>2</sub> and H<sub>2</sub>O were added in the feed all three catalyst samples kept their high activity only for the first hour. After this relatively short period, activity started to decrease smoothly and after few hours of operation (4 h) N<sub>2</sub>O conversion dropped to 65–75%, with no significant differences induced by the various catalyst pretreatments.

In an effort to regenerate the partially deactivated catalyst samples after 4 h of operation, we treated each sample at 500 °C for 1 h under the same atmosphere as the one applied for its pretreatment. As it can be seen in Fig. 3A regeneration under reducing atmosphere (5% H<sub>2</sub>/He) restored catalyst's activity to almost 100% N<sub>2</sub>O conversion. In the case of the other regeneration conditions (inert and oxidative), the catalysts' activity remained unchanged and conversion continued to drop with time-on-stream. The observed complete regeneration of the catalyst under reducing atmosphere lasted however only for ~1 h and then the conversion started to decrease smoothly again. The regeneration capability of the catalyst samples was further investigated by conducting reaction-regeneration cycles comprising 60 min reaction at 500 °C with feed containing N<sub>2</sub>O, O<sub>2</sub>, SO<sub>2</sub> and H<sub>2</sub>O and 30 min regeneration under the same atmosphere as the one applied for pretreatment of each sample. The results are shown in Fig. 3B where it can be seen that regeneration under inert and oxidative atmosphere do not affect the continuous decrease of activity (as also shown in Fig. 3A), while intermediate regenerations with H<sub>2</sub> retain catalyst's activity at conversion levels higher than 90% for a long reaction time. Further optimization of the regeneration procedure was attempted by treating the catalyst with 5% H<sub>2</sub>/He at 500 °C for very short times (ca. 12 min), when the conversion of N<sub>2</sub>O was reaching 98% (from 100%). In this way, we managed to keep the activity at ~100% for a long reaction time and reduce significantly the time necessary for complete regeneration of the catalyst (Fig. 3B).

The inability to regenerate the catalyst at 500 °C under inert (He) or oxidative (5% O<sub>2</sub>/He) atmosphere, in contrast to the reducing atmosphere (5% H<sub>2</sub>/He), required further investigation, in order to better understand the mechanism of deactivation–reactivation. We thus performed detailed characterization of the partially deactivated samples and of those after regeneration under various conditions. The XRD pattern of the catalyst sample after the reaction at 500 °C for 4 h with feed containing N<sub>2</sub>O, O<sub>2</sub>, SO<sub>2</sub> and H<sub>2</sub>O, showed the presence of only oxidized Ru species (Fig. 1d). The size of the Ru oxide particles on this sample estimated by Scherrer analysis of the XRD data (as described in Section 3.1) was ~26 nm, similar to that of the fresh oxidized or reduced Ru catalyst. In addition, the size of metallic Ru in the H<sub>2</sub>-regenerated catalyst (XRD pattern shown in Fig. 1e) was ~27 nm while the size of the Ru oxide in the O<sub>2</sub>-regenerated catalyst (XRD pattern shown in Fig. 1f) was ~28 nm. Based on these data, the lower catalytic activity of the O<sub>2</sub>-regenerated sample compared to that of the H<sub>2</sub>-regenerated sample cannot be attributed to differences in the size of Ru particles (due to possible agglomeration) since in both catalyst samples the Ru particles have similar size.

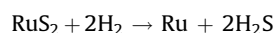
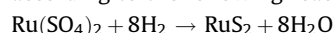
As described in the previous Section 3.2, the deactivation caused by O<sub>2</sub> and H<sub>2</sub>O is to a great extent reversible without actually affecting the properties of the catalyst, while the presence of SO<sub>2</sub> in the feed results in the formation of sulphates on Ru and the support. Since the deactivation of the catalyst is substantial after 4 h of operation (~30%, see Fig. 3A) it can be suggested that the sulphates formed on Ru (which provides the active sites) are mainly responsible for such a considerable decrease of activity.

**Table 1**  
Elemental analysis and EDS microanalysis of catalysts.

Catalyst sample	Elemental analysis (wt.%)	EDS microanalysis (% atomic ratios)		
		S	Al	Ru
Ru/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> calcined	0	94.4	5.6	–
Ru/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> deactivated <sup>a</sup>	0.63	91.8	4.7	3.5
Ru/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> regenerated with 5% O <sub>2</sub> /He	0.56	92.7	4.7	2.6
Ru/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> regenerated with 5% H <sub>2</sub> /He	0.24	94.5	4.6	0.9

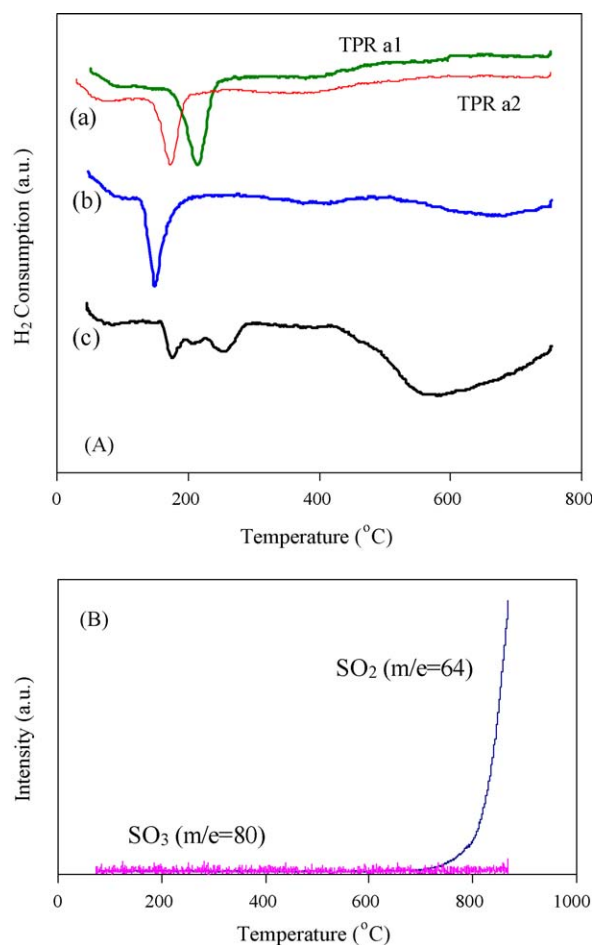
<sup>a</sup> After reaction at 500 °C for 4 h with feed: 500 ppm N<sub>2</sub>O, 5% O<sub>2</sub>, 50 ppm SO<sub>2</sub>, 10% H<sub>2</sub>O in He.

Ruthenium or aluminum sulphate phases were not identified in the XRD patterns of the deactivated catalysts (they exhibited only the diffraction peaks of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and RuO<sub>2</sub>), possibly because these phases are in very small amounts, mainly covering the external surface of RuO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> crystals. Thus, in order to determine whether S species are present on the catalyst samples, we performed EDS microanalysis and elemental analysis for S (see Section 2). From the data in Table 1 it can be seen that the catalyst sample regenerated under oxidative atmosphere contained double amounts of S (0.56 wt.%) compared to the sample regenerated under reducing atmosphere (0.24 wt.%) and very close to the S found on the deactivated sample (0.63 wt.%). The EDS microanalysis showed an even larger difference between the two regenerated catalyst samples, with the H<sub>2</sub>-regenerated sample exhibiting very small amounts of S. It is clear that the formed sulphates on the surface of the catalyst cannot be decomposed with regeneration at 500 °C under oxidative or inert atmosphere. This was further verified by the TPD-MS experiments (Fig. 4B) for the O<sub>2</sub>-regenerated catalyst sample, where it was shown that SO<sub>2</sub> started to desorb only at temperatures higher than ca. 700 °C. On the other hand, it can be suggested that in the presence of H<sub>2</sub>, Ru sulphates are converted to metallic Ru and H<sub>2</sub>S via the intermediate formation RuS<sub>2</sub> and H<sub>2</sub>O. This reaction takes place at much lower temperature, compared to the decomposition of Ru sulphates in O<sub>2</sub> or He, as it was revealed by the TPR-H<sub>2</sub> and TPD experiments that we performed on the catalyst sample regenerated with O<sub>2</sub>/He. As can be seen in Fig. 4A, a broad and relatively intense peak with maximum at ~580 °C is observed in the TPR-H<sub>2</sub> spectra of the catalyst sample regenerated with O<sub>2</sub>/He, which can be attributed to the reduction of Ru<sup>4+</sup> in Ru(SO<sub>4</sub>)<sub>2</sub> to metallic Ru, according to the following reaction steps:



In the TPR spectra of the catalyst sample regenerated with H<sub>2</sub>/He a very broad and weak peak from ~500 to 750 °C is also attributed to the above reduction scheme due to the presence of sulphates which however are in significantly lower amounts in this sample compared to the sample regenerated with O<sub>2</sub>/He.

With regard to the TPR peaks that correspond to the reduction of oxidized Ru on the surface of the catalyst, the parent calcined sample showed a sharp and intense peak at ~215 °C due to reduction of Ru<sup>4+</sup> in RuO<sub>2</sub> to metallic Ru during the 1st TPR experiment (curve TPR a1), while in a subsequent 2nd TPR experiment (re-oxidation at 500 °C followed by TPR-H<sub>2</sub>) this peak was shifted to lower temperature (at ~170 °C; curve TPR a2). This behavior has been also reported previously [38] and could be attributed to the weaker interaction of the re-oxidized Ru particles with surface oxygen atoms of the alumina support compared to the RuO<sub>2</sub> particles formed during calcination of the fresh impregnated-dried sample. Stronger interfacial interactions between RuO<sub>2</sub> and aluminum support can induce higher reduction temperatures for

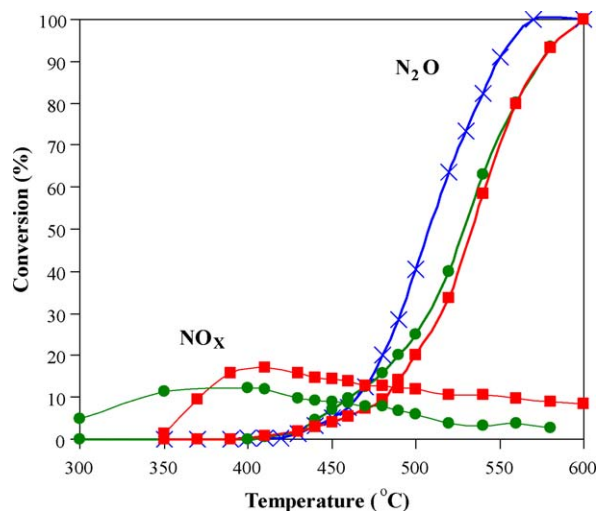


**Fig. 4.** (A) TPR-H<sub>2</sub> spectra of: (a) Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> calcined (after impregnation and drying) at 500 °C for 4 h in air (spectrum TPR a1) and after a second consecutive oxidation at 500 °C with O<sub>2</sub>/He (TPR a2), (b) Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> after 4 h reaction at 500 °C with N<sub>2</sub>O/O<sub>2</sub>/SO<sub>2</sub>/H<sub>2</sub>O/He and regenerated with 5% H<sub>2</sub>/He, (c) Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> after 4 h reaction at 500 °C with N<sub>2</sub>O/O<sub>2</sub>/SO<sub>2</sub>/H<sub>2</sub>O/He and regenerated with 5% O<sub>2</sub>/He. (B) TPD-MS with He of catalyst sample regenerated with 5% O<sub>2</sub>/He (same as in case A(c) above).

Ru<sup>4+</sup>, as has been also previously identified [33,39]. In the case of H<sub>2</sub>-regenerated sample, the peak assigned to reduction of RuO<sub>2</sub> has a maximum at ~150 °C which is close to the behavior of the parent calcined sample in the 2nd TPR experiment. On the other hand, the O<sub>2</sub>-regenerated sample exhibits three peaks at ~175, 210 and 255 °C. The first two peaks are clearly attributed to the reduction of Ru<sup>4+</sup> in RuO<sub>2</sub> to metallic Ru while the third peak at 255 °C could be associated with the reduction of Ru at higher oxidation states, such as in RuO<sub>3</sub> [35].

### 3.4. Effect of NO<sub>x</sub> on N<sub>2</sub>O decomposition

Nitrogen oxides (NO<sub>x</sub>) are toxic gases, harmful to human health and the environment. NO<sub>x</sub> and N<sub>2</sub>O coexist in the flue gases of many industrial processes, such as fluidized bed combustion and chemical processes associated with the production and use of nitric acid [4–6,13–17]. The two areas of application differ in various aspects, such as in N<sub>2</sub>O concentration and in the presence of other “poisonous” gases. In this section, we investigate, how the addition of NO<sub>x</sub> in the feed gas containing O<sub>2</sub>, SO<sub>2</sub> and H<sub>2</sub>O, which are commonly found in combustion off-gases, affects the performance of Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst on N<sub>2</sub>O decomposition. These results are shown in Fig. 5 from where it becomes evident that addition of NO<sub>x</sub> in the feed has a relatively small additional

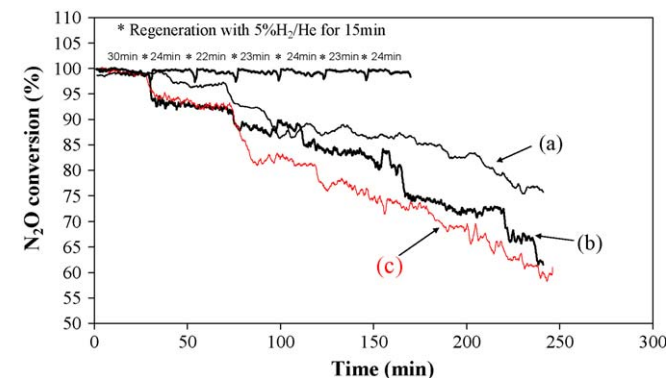


**Fig. 5.** Effect of NO<sub>x</sub> concentration on the catalytic activity of Ru/γ-Al<sub>2</sub>O<sub>3</sub> in N<sub>2</sub>O decomposition for various feeds: (×) 500 ppm N<sub>2</sub>O, 5% O<sub>2</sub>, 50 ppm SO<sub>2</sub>, 10% H<sub>2</sub>O, 0 ppm NO<sub>x</sub> in He, (●) 500 ppm N<sub>2</sub>O, 5% O<sub>2</sub>, 50 ppm SO<sub>2</sub>, 10% H<sub>2</sub>O, 500 ppm NO<sub>x</sub> in He, (■) 500 ppm N<sub>2</sub>O, 5% O<sub>2</sub>, 50 ppm SO<sub>2</sub>, 10% H<sub>2</sub>O, 1000 ppm NO<sub>x</sub> in He. Total flow rate: 500 cm<sup>3</sup>/min; catalyst weight: 0.5 g; GHSV: 56,000 h<sup>-1</sup>.

inhibition effect compared to that of the mixture O<sub>2</sub> + SO<sub>2</sub> + H<sub>2</sub>O. With increasing NO<sub>x</sub> concentration from 500 to 1000 ppm no further deactivation was observed. The NO<sub>x</sub> conversion over the catalyst was relatively low (<20%) for both concentrations and took place over a broad temperature range (350–600 °C).

The effect of NO<sub>x</sub> addition in the feed containing O<sub>2</sub>, SO<sub>2</sub> and H<sub>2</sub>O on catalyst's durability was also studied for both NO<sub>x</sub> concentrations (500 and 1000 ppm). As it can be seen in Fig. 6, NO<sub>x</sub> enhances the deactivation of the catalyst over time and after 4 h of operation the conversion of N<sub>2</sub>O has dropped to ~60% (for both NO<sub>x</sub> concentrations) compared to the ~75% conversion in the absence of NO<sub>x</sub>. Based on the results described in Section 3.3, regeneration of the catalyst under reducing atmosphere was also applied in this case. The procedure was optimized and as it can be seen from the results in Fig. 6, with short time regenerations (15 min each) when the conversion of N<sub>2</sub>O was dropping to ~98% (from 100%), we managed to keep N<sub>2</sub>O conversion (in the presence of O<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>O and NO<sub>x</sub>) at 100% for relatively long reaction time.

The observed inhibition effect of NO<sub>x</sub> in the feed gas mixture containing "poisonous" gases (O<sub>2</sub>, SO<sub>2</sub> and H<sub>2</sub>O), has also been found previously [4–6], for various catalysts based on Ru and Rh and it was attributed to competitive adsorption with N<sub>2</sub>O for the same active

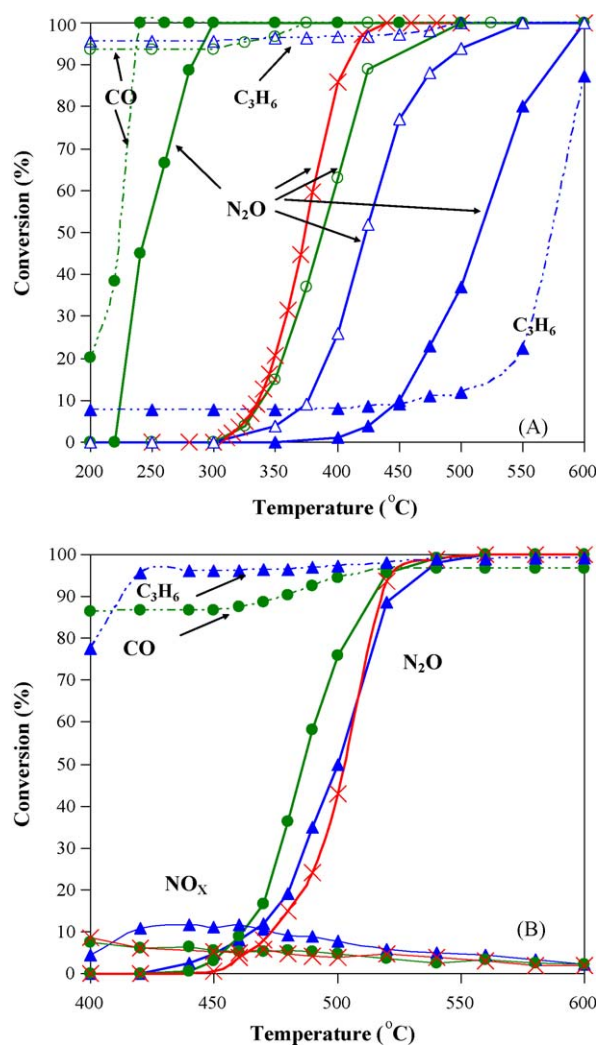


**Fig. 6.** Effect of NO<sub>x</sub> addition on N<sub>2</sub>O conversion activity vs. time-on-stream for Ru/γ-Al<sub>2</sub>O<sub>3</sub> catalysts and effect of frequent regenerations in reductive atmosphere (5% H<sub>2</sub>/He), for various feeds: (a) 500 ppm N<sub>2</sub>O, 5% O<sub>2</sub>, 50 ppm SO<sub>2</sub>, 10% H<sub>2</sub>O, 0 ppm NO<sub>x</sub> in He, (b) 500 ppm N<sub>2</sub>O, 5% O<sub>2</sub>, 50 ppm SO<sub>2</sub>, 10% H<sub>2</sub>O, 500 ppm NO<sub>x</sub> in He, (c) 500 ppm N<sub>2</sub>O, 5% O<sub>2</sub>, 50 ppm SO<sub>2</sub>, 10% H<sub>2</sub>O, 1000 ppm NO<sub>x</sub> in He. Reaction temperature: 500 °C; total flow rate: 500 cm<sup>3</sup>/min; catalyst weight: 1 g; GHSV: 19,500 h<sup>-1</sup>.

sites and to possible deactivation of catalyst through nitrite or nitrate formation [5]. However in the case of other catalytic systems such as Fe/ZSM-5 [5,6] and Fe-ferrierite [14] a promoting effect of NO<sub>x</sub> addition on N<sub>2</sub>O conversion has been observed.

### 3.5. Effect of reducing agent on N<sub>2</sub>O conversion

In Section 3.2 (Fig. 2) it was shown that the metallic (reduced) Ru particles are slightly more active in the decomposition of pure N<sub>2</sub>O (in the absence of O<sub>2</sub>, SO<sub>2</sub> and H<sub>2</sub>O), compared to the catalysts with oxidized Ru. Based on that result, we investigated the effect of addition of a reducing agent (CO or C<sub>3</sub>H<sub>6</sub>) in the feed during N<sub>2</sub>O conversion. The respective results are shown in Fig. 7A. In the experiments where the feed consisted only of N<sub>2</sub>O in He (500 ppm N<sub>2</sub>O/He) the presence of CO (1000 ppm) as reducing agent enhanced the decomposition activity of Ru/γ-Al<sub>2</sub>O<sub>3</sub> significantly, since complete N<sub>2</sub>O conversion was achieved at ~280 °C while in the absence of CO this temperature was higher (440 °C). Kawi et al.



**Fig. 7.** (A) Effect of addition of reducing agents (CO, C<sub>3</sub>H<sub>6</sub>) on N<sub>2</sub>O conversion over Ru/γ-Al<sub>2</sub>O<sub>3</sub> catalyst for various feeds: (×) 500 ppm N<sub>2</sub>O in He (no reductant), (●) 500 ppm N<sub>2</sub>O, 1000 ppm CO in He, (▲) 500 ppm N<sub>2</sub>O, 1000 ppm C<sub>3</sub>H<sub>6</sub> in He, (○) 500 ppm N<sub>2</sub>O, 2% O<sub>2</sub>, 1000 ppm CO in He, (△) 500 ppm N<sub>2</sub>O, 2% O<sub>2</sub>, 1000 ppm C<sub>3</sub>H<sub>6</sub> in He. Total flow rate: 500 cm<sup>3</sup>/min; catalyst weight: 0.5 g; GHSV: 56,000 h<sup>-1</sup>. (B) Effect of addition of reducing agents (CO, C<sub>3</sub>H<sub>6</sub>) on N<sub>2</sub>O and NO<sub>x</sub> conversion over Ru/γ-Al<sub>2</sub>O<sub>3</sub> catalyst for feeds containing "poisonous" gases and NO<sub>x</sub>: (×) 500 ppm N<sub>2</sub>O, 2% O<sub>2</sub>, 50 ppm SO<sub>2</sub>, 10% H<sub>2</sub>O, 500 ppm NO<sub>x</sub> in He (no reductant), (●) 500 ppm N<sub>2</sub>O, 2% O<sub>2</sub>, 50 ppm SO<sub>2</sub>, 10% H<sub>2</sub>O, 500 ppm NO<sub>x</sub>, 1000 ppm CO in He, (▲) 500 ppm N<sub>2</sub>O, 2% O<sub>2</sub>, 50 ppm SO<sub>2</sub>, 10% H<sub>2</sub>O, 500 ppm NO<sub>x</sub>, 1000 ppm C<sub>3</sub>H<sub>6</sub> in He. Total flow rate: 500 cm<sup>3</sup>/min; catalyst weight: 0.5 g; GHSV: 56,000 h<sup>-1</sup>.



[35] investigated also the effect of CO on the decomposition of  $\text{N}_2\text{O}$  on Ru/MCM-41 catalysts and observed the same positive effect of CO on catalyst's activity. They attributed this enhancement to the removal of surface oxygen species generated during the decomposition of adsorbed  $\text{N}_2\text{O}$  on the surface active sites by CO. Addition of  $\text{O}_2$  (2%) in the feed resulted in the decrease of  $\text{N}_2\text{O}$  conversion activity to a level similar to that in the absence of CO (Fig. 7A). This behaviour is attributed to the almost complete oxidation of CO to  $\text{CO}_2$  at temperatures as low as 200 °C (Fig. 7A). On the other hand, when the feed contained all gases (results shown in Fig. 7B), e.g.  $\text{O}_2$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{NO}_x$ , the presence of CO in the feed induced a slightly higher catalytic activity compared to that observed in the absence of CO. This performance is related with the partial inhibition of CO oxidation to  $\text{CO}_2$  since as it can be seen in Fig. 7B, there is still some CO available at temperatures as high as 500 °C. Presumably, a portion of  $\text{O}_2$  is consumed in the transformation of the other "poisonous" gases, i.e.  $\text{NO}_x$  and  $\text{SO}_2$ , thus leaving more CO to act as reductant. Nevertheless, from the above data it can be suggested that the relative amount (percent) of  $\text{O}_2$  in the feed is a very important factor in determining the  $\text{N}_2\text{O}$  conversion activity, both in  $\text{N}_2\text{O}$  decomposition and in  $\text{N}_2\text{O}$  reduction (when a reductant is present in the feed). In the latter case, the  $\text{O}_2$  concentration in relation with the oxidation activity of the metallic catalyst determines the amount of reductant that will be left available for the conversion of  $\text{N}_2\text{O}$ .

In contrast to CO, addition of  $\text{C}_3\text{H}_6$  (1000 ppm) in the feed resulted in a dramatic decrease of the conversion activity of pure  $\text{N}_2\text{O}$  (100% conversion was achieved at temperatures as high as 600 °C), as can be seen in Fig. 7A. This behaviour of propylene when used as reductant in the conversion of nitrogen oxides, i.e. suppressing the conversion in the absence of  $\text{O}_2$ , has been also previously identified in  $\text{N}_2\text{O}$  reduction by Ru/ $\gamma\text{-Al}_2\text{O}_3$  catalysts [19] and in NO reduction by Pt/ $\text{Al}_2\text{O}_3$  catalysts [40]. On the other hand, the activity of the Rh/ $\text{Al}_2\text{O}_3$  catalysts was enhanced by the addition of  $\text{C}_3\text{H}_6$  (in the absence of  $\text{O}_2$ ) in both the above studies. In the present work, as it can be seen in Fig. 7A, the very low conversion of  $\text{N}_2\text{O}$  up to ca. 450 °C is accompanied by low conversion of propylene which does not exceed 10% at 500 °C. It can thus be suggested that in the present catalytic system of Ru/ $\gamma\text{-Al}_2\text{O}_3$  and  $\text{N}_2\text{O}$  (in the absence of  $\text{O}_2$ ) propylene does not participate in the  $\text{N}_2\text{O}$  conversion reaction and furthermore blocks the active sites of Ru onto which  $\text{N}_2\text{O}$  decomposition could otherwise have occurred. Addition of  $\text{O}_2$  (2%) in the feed led to remarkable improvement in activity, which, however, was still lower than that in the pure  $\text{N}_2\text{O}$  decomposition, as can be seen in Fig. 7A. This improvement can be attributed mainly to the consumption/oxidation of  $\text{C}_3\text{H}_6$  by  $\text{O}_2$  to  $\text{CO}_2$  (Fig. 7A), with the remaining  $\text{O}_2$  acting as an inhibitor in the  $\text{N}_2\text{O}$  decomposition reaction. However, when all the gases were present in the feed (e.g.  $\text{O}_2$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{NO}_x$ ) the  $\text{N}_2\text{O}$  conversion activity was almost similar to that measured in the absence of  $\text{C}_3\text{H}_6$  (Fig. 7B). As in the case of CO, it can be suggested that a portion of  $\text{O}_2$  is consumed for reaction with the other gases, i.e.  $\text{NO}_x$  and  $\text{SO}_2$ , thus minimizing its negative effect on the  $\text{N}_2\text{O}$  conversion activity.

Finally, the use of either CO or  $\text{C}_3\text{H}_6$  had also minor effect on converting/reducing the  $\text{NO}_x$  when present in the feed (Fig. 7B). As it was explained above, both the reducing agents were almost completely converted to  $\text{CO}_2$  at temperatures between 425 and 500 °C, in the presence of 2%  $\text{O}_2$  in the feed, thus leaving no significant amounts of CO or  $\text{C}_3\text{H}_6$  available for the reduction of  $\text{N}_2\text{O}$  and/or  $\text{NO}_x$ .

#### 4. Conclusions

Pretreatment of impregnated-calcined Ru/ $\gamma\text{-Al}_2\text{O}_3$  catalyst under inert, oxidative or reducing atmosphere has a minor effect on its activity and stability in the decomposition of  $\text{N}_2\text{O}$  in the

presence of various gases, such as  $\text{O}_2$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{NO}_x$ , typically found in combustion processes. A slight improvement of the decomposition activity of pure  $\text{N}_2\text{O}$  was observed with the  $\text{H}_2$ -pretreated catalyst (metallic Ru), owing to a cyclic oxidation–reduction pathway of metallic Ru. Addition of  $\text{O}_2$  or  $\text{H}_2\text{O}$  decreased the decomposition activity reversibly while on the other hand, addition of  $\text{SO}_2$  resulted in pronounced and irreversible deactivation of the catalyst due to the formation of stable sulphates, mainly those on Ru $_2\text{O}_3$  surface. TPR- $\text{H}_2$  and TPD-MS experiments revealed that these sulphates can be more easily removed by regeneration under reducing ( $\text{H}_2$  in He) atmosphere at temperatures of ca. 500 °C, compared to the oxidative or inert regeneration which required very high temperatures (i.e. >700 °C) in order to decompose the sulphates. In the former case, a reduction mechanism is involved via intermediate formation of RuS $_2$  which is subsequently transformed to metallic Ru (reduction of Ru $^{4+}$ ) and  $\text{H}_2\text{S}$ . Frequent and short-time regenerations of partially deactivated Ru/ $\gamma\text{-Al}_2\text{O}_3$  catalysts under reducing atmosphere can retain the  $\text{N}_2\text{O}$  conversion activity very high ( $\geq 98\%$ ) for long reaction times. The presence of CO as reducing agent enhances greatly the conversion/reduction of pure  $\text{N}_2\text{O}$ , while both CO and  $\text{C}_3\text{H}_6$  have almost no effect on  $\text{N}_2\text{O}$  conversion in the presence of  $\text{O}_2$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{NO}_x$ , mainly because they are oxidized at relatively low temperatures with feeds containing relatively high  $\text{O}_2$  concentrations (such as 2% or 5%  $\text{O}_2$  used in this study).

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